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13. ABSTRACT *(Maximum 200 Words)*

High-temperature superconducting conductors for power application have been identified as a critical enabling technology for future Air Force systems. Work on the materials science and factors limiting current carry capacity of 123 YBCO coated conductor materials are reported. A new model of the high-rate electron-beam coevaporation of 123 YBCO has been developed based on our experiments. It now appears that the process involves an amorphous precursor that is subsequently oxidized. Also the crystallization of the film appears to involve a liquid flux of BaCuOx. The first successful route of synthesis of 248 YBCO thin films has also been developed. We have also carried out scanning tunneling spectroscopy on the surfaces of 2212 BSCCO that reveal the presence of nanoscale inhomogeneities of the superconducting energy gap that could be a source of vortex pinning and hence the critical current in this material. A scanning tunneling potentiometer system has been constructed. This system has yielded the first transport measurements of a complete oxide material on a nanometer scale.

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Final Report

MATERIALS SCIENCE AND MATERIALS PHYSICS IN SUPPORT OF HIGH TEMPERATURE SUPERCONDUCTING COATED CONDUCTOR DEVELOPMENT

AFOSR Grant F49620-01-1-0103-P0004
For the period 5 December, 2000 to 4 March, 2004

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Final Report

MATERIALS SCIENCE AND MATERIALS PHYSICS IN SUPPORT OF HIGH TEMPERATURE SUPERCONDUCTING COATED CONDUCTOR DEVELOPMENT

Introduction

High-temperature superconducting conductors for power application have been identified as a critical enabling technology for future Air Force systems. They also are of interest for commercial applications. This program is focused on the materials science and materials physics of these conductors, specifically the materials science of high-rate, electron-beam coevaporated coated conductors and the physical processes governing their current carrying capacity. In the case of the latter, new nanoscale scanning probes are being developed. Alternative superconductors for possible substitution for the leading candidate 123 YBCO are also under investigation. The overall goal is to provide the scientific basis on which high-temperature superconducting coated conductors can be manufactured cheaply and with optimized performance.

Materials Science of 123 YBCO Relevant to High-Rate Deposition

Successful coated conductor applications require grain-boundary-free, single-crystal-like thin films deposited economically on kilometer lengths of tape. This requires epitaxial film growth on an unprecedented size scale. As we have shown in earlier analyses, electron-beam coevaporation is one of a very few deposition technologies capable of the very high rates required to achieve the necessary low costs. Our original concept involved an in-situ growth approach in which the 123 YBCO was to be formed directly by coevaporation of the cations in the presence of activated oxygen. The required molecular oxygen pressure to form 123 YBCO is simply too high to be able to maintain the high vacuum conditions required by an electron beam deposition process.

In order to provide the required activated oxygen, we developed a high-flux atomic oxygen source using a high power microwave cavity plasma. The atomic oxygen is generated in the cavity and then transported to the deposition system though a Teflon-coated delivery tube. The flux of atomic oxygen can be monitored using a UV atomic absorption technique, also developed by us. In this case the needed UV light from a hollow cathode plasma source is transported in and out of our deposition system using UV light pipes.

Using these tools we successfully grew in-situ 123 YBCO thin films. Remarkably, we also found that we could produce 123 YBCO films even without the atomic oxygen source. Given the known phase stability of 123 YBCO, this result was

confounding and obviously required a new model of the deposition process. This necessity led to the conjecture that somehow atomic oxygen was being generated in our system itself. This in turn led to the theory that the atomic oxygen was being generated by the electron beam impinging of the oxidized surface of our Ba source through processes understood in other contexts. Unfortunately, by this time the UV plasma source for our atomic oxygen atomic absorption detection equipment had failed, and it was not possible to test directly for this incidental atomic oxygen.

More recently, we have come to realize that an incidental source of atomic oxygen may not be necessary in our process. Under our AF MURI program, we developed an FTIR system for the purposes of measuring the absolute temperature of a growing film. This same system permits us to monitor in situ and in real time the optical properties of a growing film. Under this program, we have been applying the FTIR technique to the growth of our 123 YBCO films. The results are striking. Based on the observed optical spectra, it seems that in fact we are not growing 123 YBCO in situ but, rather, are growing a precursor film that subsequently converts to 123 YBCO upon oxidation at high pressure. If true, this is a striking result that changes fundamentally our process model. We intend to follow up this work vigorously.

Other studies are leading us to equally important insights into our deposition process. These are based on physical and structural characterization of our films. Depth profiling (under our MURI program) of the critical current density and resistivity of some of our 123 YBCO films showed that the films produced with our process consist of a lower 123 YBCO layer that is insulating (presumably oxygen O_6) and carried no critical current and an upper 123 YBCO layer that has good metallic conductivity (presumably oxygen O_7) and carries a very high critical current density. This bilayer structure was confirmed by TEM on some samples. The TEM further showed that the lower layer was a single crystal like, while the upper layer was highly faulted. TEM and x-ray diffraction work showed that there also was a polycrystalline BaCuOx layer to top of the 123 YBCO bilayer.

The microstructure of the lower two layers explains the depth profiling experiments. It is well known that it is very hard to fully oxygenate single-crystal 123 YBCO, hence its insulating nature. By contrast the faulted layer oxygenates easily and, moreover, obviously has good pinning. The presence of the BaCuOx layer also provided an important clue to the mechanisms of growth that led to the primary bilayer structure, and, in particular, the observed single crystal nature of the lower layer. Such single-crystal-like growth is very hard to understand on the basis of normal vapor-deposited thin film growth mechanisms. It requires very fast kinetics such as obtained in growth from a liquid. The following model has emerged.

It appears that the film growth is actually via a BaCuOx liquid flux from which the 123 YBCO precipitates, leaving some residual flux on the top. The resultant crystal grows epitaxially on the single-crystal substrate. In essence what we have is a form of liquid phase epitaxy in an electron-beam co-evaporation process. Further evidence for the presence of a liquid is the dendritic growth morphology of some of our films that

were held a long time at high temperature during processing. To be self-consistent, this liquid growth model requires a modification of the existing phase diagram of the YBCO system under the conditions of our film growth. Specifically, there must be an equilibrium BaCuOx phase with a tie line to 123 YBCO. Subsequent work by other groups provides further evidence for this liquid phase and its importance in achieving high rate growth.

In summary, under this program very substantial progress has been made in understanding the material science of growth of 123 YBCO films that provide insight not only into our high-rate, electron-beam coevaporation process, but likely other processes as well.

Synthesis of 248 YBCO Thin Films

The 248 phase of YBCO was discovered at Stanford in the early days of research on the high-Tc superconductors. It has the interesting feature that it is superconducting at its stoichiometric oxygen concentration. In principle, this suggests that 248 YBCO may have fewer problems with oxygen depleted grain boundaries, which are a known source of critical current degradation of 123 YBCO. The downside is that heretofore it has not been possible to synthesize this phase in thin film form due to the very high oxygen pressures required – even higher than 123 YBCO. As part of this program, we have been exploring new ways to synthesize thin films of this material.

Our approach uses pulsed laser deposition (PLD) rather then electron-beam coevaporation because of its greater simplicity and flexibility. The problem was to achieve the necessary high oxygen pressures for an in situ deposition technique. Initially, we took a very direct approach and built a system in which the film was alternately moved between the PLD plasma (in which essentially the cations are deposited) and a high oxygen pressure pocket into which oxygen was injected and in which the compound is actually formed.

While the hardware worked to achieve high oxygen pressure, it was plagued with mechanical problems and subsequently abandoned. However, during the learning process it was found that 248 YBCO could be synthesized starting from an amorphous YBCO oxide precursor deposited using PLD that is subsequently processed at high temperature and oxygen pressure to form 248 YBCO thin films. Optimization of both the conditions of growth of the precursor and the subsequent oxygen processing has yielded twin-free, single-crystal-like epitaxial thin films on SrTiO3 substrates. This is remarkable. Still, it works. As we look ahead, it will be of interest to study in detail the physical properties of these films, in particular the critical current densities of the grain boundaries.

Remarkably, similar to 123 YBCO, we find that an effective route to thin film synthesis of 248 YBCO is through an amorphous YBCO precursor. The subsequent processing is different in the two cases, however. Still, we wonder how generally this approach might be applied to complex oxides. Of course, using precursors to make 123

YBCO is not a completely new idea. The BaF process being developed at ORNL does just this. The difference here is that no F is involved. Also, in the case of electron-beam coevaporation, very high rates are possible.

Scanning Probes

Another theme in our program is the development of scanning probes capable of physical characterization of coated conductors on unprecedented small length scales. Under this program, we initially had two thrusts. The first involved using scanning tunneling spectroscopy (STS) to study the cuprate superconductors. The second involved the development of scanning tunneling potentiometry (STP) as a practical tool for studying transport at short length scales in coated conductors.

STS studies were carried out on cleaved surfaces of the high temperature superconductor 2212 BSCO. This material was chosen initially over 123 YBCO because if has such a nice surface for STS. Like many researchers doing similar work, we were able to see the superconducting energy gap. More importantly in the context of practical superconductivity, we found that there were inhomogeneities in both the size and the nature of the tunneling spectra over nanometer length scales.. The significance of this result to the AFOSR is that nanoscale inhomogeneities are a natural source of the vortex pinning necessary in practical superconductors to achieve high critical current densities. These STS results have been controversial in some circles, but they seem to be holding up well and are now widely cited. Still, it is difficult to do such studies on the material of practical interest, 123 YBCO. Also the researcher involved in the work was disinclined to pursue the practical implications of the results, and so the work was transferred to other support.

In the case of STP, a practical measurement system had to be built from scratch. The concept of STP had been demonstrated (including by ourselves), but no one had built up a truly practical system. This turned out to be a major engineering undertaking. There were two major problems. The first was to build up a real-time computer controlled system that could automate the complicated and delicate measurement sequences required to alternately obtain STM topography data and STP data without computer or tunneling tip crashes. These problems were solved and a quite powerful and convenient data taking system now is available.

The second was to build a STP head that could work over wide areas while maintaining nanometer scale resolution locally and that could work at the desired low temperatures and high magnetic fields necessary for coated conductor studies. The STP head has been designed and built, and a superconducting magnet system into which it can be installed has been acquired. We have postponed assembling the ultimate system, however, while studying a variety of material at room temperature, in order to gain experience and ensure that our computer controllers perform as we desire. This effort has been successful. We have acquired good topographic and potentiometric images on granular gold films and on amorphous In-oxide films. These materials were selected because they have relatively inert surfaces and, of course, because they are interesting. In

the case of the In-oxide films, potentiometric features on the sub-10nm scale are evident. To our knowledge these are the first automated transport measurements ever on a complex oxide thin film on this length scale. We also have begun working on 123 YBCO thin films relevant to coated conductors. Here the surface issues are serious and will require a concerted effort.

Other Work

In addition to the work described above, a few smaller efforts were undertaken under this program. We wrote up for publication our earlier work on electrochemical thin film oxygen sensors for thin films deposition work. We also wrote up for publication our work on the development of an in-situ, real-time XPS system suitable for working in the high vacuum pressures needed for thin film synthesis of complex oxides. We also explored a means for synthesizing MgB2 thin films in-situ and studied the transport properties of the resultant films. Finally, some papers providing scientific and historical perspective on various aspects of superconductivity were prepared and published.

PERSONNEL SUPPORTED

Faculty – Professors M.R. Beasley and T.H. Geballe
Senior Research Scientist – Dr. R.H. Hammond
Postdoctoral Researchers – Dr. Gert Koster
Students (primary) – J.-U. Huh, M. Rozler
Students (partial) – J.-H. Lee (Visiting Graduate Student from Korea)

PUBLICATIONS

Accepted:

1. I. Bozovic, G. Logvenov, M.A.J. Verhoeven, P. Caputo, E. Goldobin, and T.H. Geballe, "No mixing of superconductivity and antiferromagnetism in a high-temperature superconductor," *Nature* **422**, 873 (2003).

2. T.H. Geballe, "Super Boron," in Perspectives: Superconductivity, *Science* **293**, 223 (2001).

3. T.H. Geballe, "Zachary Fisk," *Physics B* **318**, 52 (2002).

4. C. Howald, P. Fournier, and A. Kapitulnik, "Inherent Inhomogeneities in Tunneling Spectra of BSCCO Crystals in the Superconducting State," *Physical Review B* **64**, 100504 (2001).

5. W. Jo, M.R. Beasley, and R.H. Hammond, "Anisotropy and critical current density of MgB_2 thin films grown *in-situ* by molecular beam epitaxy," *IEEE Transactions on Applied Superconductivity* **13**, 3257 (2002).

6. W. Jo, J-U. Huh, T. Ohnishi, A.F. Marshall, M.R. Beasley, and R.H. Hammond, "In-situ growth of superconducting MgB_2 thin films with preferential orientation by molecular beam epitaxy," *Applied Physics Letters* **80**, 3563 (2002).

7. M.A. Kelly, M.L. Shek, P. Pianetta, T.M. Gur, and M.R. Beasley, "In-situ x-ray photoelectron spectroscopy for thin film synthesis monitoring," *Journal of Vacuum Science and Technology A*, **19**, 2127 (2001).

8. V. Oganesyan, S. Kivelson, T. Geballe, and B. Moyzhes, "Josephson tunneling spectroscopy of negative-*U* centers," *Physical Review B* **65**, 172504 (2002).

9. T. Ohnishi, J.-U. Huh, R.H. Hammond, and W. Jo, "High rate in-situ YBCO film growth assisted by liquid phase," *Journal of Materials Research* **19**, 977 (2004).

10. E. van Setten, T.M. Gur, D. Blank, J.C. Bravman, and M.R. Beasley, "Miniature Nernstian Oxygen Sensor for Deposition and Growth Environments," *Review of Scientific Instruments* **73**, 156 (2002).

INTERACTIONS AND TRANSITIONS

Meetings:

M.R. Beasley

- Banff Network and Nanoscale Workshop, Banff, Canada, August 21 – 26, 2001. Invited lecture.
- Los Alamos National Laboratory, fall 2001. Lecture
- Oak Ridge National Laboratory, fall 2001. Lecture

R. Hammond

- Electrochemical Society, Orlando, FL, October 12-16, 2003. Invited paper

Jeong-uk Huh

- Materials Research Society Fall Meeting, Boston, MA, December 2003, Invited lecture.

T.H. Geballe

- 10th International Workshop on Oxide Electronics, Augsburg, Germany, September 2005, invited lecture "Paying attention to Tc," with B. Moyzhes.

Consulting/Advisory Functions:

Transitions:

We are working closely and on a regular basis with the Los Alamos National Laboratory coated conductor group on the materials science of high-rate, electron-beam coevaporation of 123 YBCO.

NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES

None during the reporting period.

HONORS/AWARDS

None during the reporting period.